

# Coral reefs modify their seawater carbon chemistry – implications for impacts of ocean acidification

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## Abstract

Reviews suggest that the biogeochemical threshold for sustained coral reef growth will be reached during this century due to ocean acidification caused by increased uptake of atmospheric CO<sub>2</sub>. Projections of ocean acidification, however, are based on air-sea fluxes in the open ocean, and not for shallow-water systems such as coral reefs. Like the open ocean, reef waters are subject to the chemical forcing of increasing atmospheric pCO<sub>2</sub>. However, for reefs with long water residence times, we illustrate that benthic carbon fluxes can drive spatial variation in pH, pCO<sub>2</sub> and aragonite saturation state ( $\Omega_a$ ) that can mask the effects of ocean acidification in some downstream habitats. We use a carbon flux model for photosynthesis, respiration, calcification and dissolution coupled with Lagrangian transport to examine how key groups of calcifiers (zooxanthellate corals) and primary producers (macroalgae) on coral reefs contribute to changes in the seawater carbonate system as a function of water residence time. Analyses based on flume data showed that the carbon fluxes of corals and macroalgae drive  $\Omega_a$  in opposing directions. Areas dominated by corals elevate pCO<sub>2</sub> and reduce  $\Omega_a$ , thereby compounding ocean acidification effects in downstream habitats, whereas algal beds draw CO<sub>2</sub> down and elevate  $\Omega_a$ , potentially offsetting ocean acidification impacts at the local scale. Simulations for two CO<sub>2</sub> scenarios (600 and 900 ppm CO<sub>2</sub>) suggested that a potential shift from coral to algal abundance under ocean acidification can lead to improved conditions for calcification in downstream habitats, depending on reef size, water residence time and circulation patterns. Although the carbon fluxes of benthic reef communities cannot significantly counter changes in carbon chemistry at the scale of oceans, they provide a significant mechanism of buffering ocean acidification impacts at the scale of habitat to reef.

**Keywords:** aragonite saturation, calcification, carbon dioxide, coral reef, Great Barrier Reef, ocean acidification

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## Introduction

Ocean acidification is the consequence of increasing CO<sub>2</sub> concentrations in the atmosphere, equilibrating with dissolved CO<sub>2</sub> in the ocean surface (Caldeira & Wickett, 2003; Sabine *et al.*, 2004) and inducing a decrease in pH and carbonate ion concentration (Caldeira & Wickett, 2003). It has been shown to decrease the calcification rate of most calcifying organisms in the sea (Kleypas *et al.*, 2006; Hendriks *et al.*, 2010; Kroeker *et al.*, 2010). One ecosystem that appears to be particularly susceptible to ocean acidification is coral reefs, whose existence depends on their ability to build calcium carbonate structures (Kleypas & Langdon, 2006). Current ocean acidification models predict that the biogeochemical threshold for sustained coral reef growth will be reached within 3–4 decades (Hoegh-Guldberg *et al.*, 2007; Silverman *et al.*, 2009). One caveat of such

predictions, however, is the assumption that reef waters acidify at a pace similar to ocean surface waters. It has long been established that the carbon chemistry of reef water varies over the course of the day and between tidal cycles (Smith, 1973; Kayanne *et al.*, 1995; Bates *et al.*, 2001; Anthony *et al.*, 2008) and spatially between upstream and downstream habitats (Barnes, 1983; Gattuso *et al.*, 1996). However, the implications of short-term temporal and spatial variation in carbon chemistry of reef water have only recently received attention in the context of ocean acidification (Yates & Halley, 2006; Andersson *et al.*, 2009; Bates *et al.*, 2010). Here, we examine analytically how the benthic carbon fluxes of contrasting reef community types, characterized by corals and non-calcifying macroalgae, modify the carbon chemistry of reef water on shallow-water systems. Our analyses are based on experimental flume data and a one-dimensional water transport model. Field validation of the model is provided in an accompanying paper (Kleypas *et al.*, 2011). Lastly, we examine how precipitation/dissolution of calcium carbonate

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and photosynthesis/metabolism of benthic reef communities of varying composition will interact with ocean acidification scenarios on shallow reefs with long water residence times and what the implications are likely to be for carbon chemistry patterns at the scale of habitats to reef systems.

## Methods

### Biological drivers

The processes largely responsible for carbon chemistry variation in reef waters are the basic life functions of the sessile benthic community: photosynthesis respiration and calcification and dissolution of calcium carbonate ( $\text{CaCO}_3$ ). Photosynthesis uses inorganic carbon ( $\text{CO}_2$  or bicarbonate, depending on the species) as substrate, and respiration by any oxygenic organism releases  $\text{CO}_2$ . Calcification takes up inorganic carbon and releases  $\text{CO}_2$ , and dissolution of calcium carbonate occurs as the reverse process (Gattuso *et al.*, 1995; Kleypas & Langdon, 2006; Jury *et al.*, 2010). The benthic carbon fluxes of  $\text{CO}_2$ , bicarbonate and carbonate ions are therefore functions of the composition of the benthic community and the environmental factors (light, water flow, temperature etc.) driving primary productivity, calcification and dissolution rates. The net changes in the  $\text{CO}_2$ -system of reef waters, such as changes in pH and/or aragonite saturation state ( $\Omega_a$ ), are a function of the ratio of organic net productivity (i.e. net photosynthesis) to net community calcification. Specifically, a high net rate of photosynthesis acts to draw down carbon (as  $\text{CO}_2$ ) from the total pool of inorganic carbon ( $C_T$ ) during the day (Suzuki *et al.*, 1995; Gattuso *et al.*, 1999), whereas nighttime respiration releases  $\text{CO}_2$ . Conversely, calcification consumes carbonate ions, which lower both  $C_T$  and total alkalinity ( $A_T$ ). The net result of these two carbon-consuming processes on the  $\Omega_a$  of reef waters is thus determined by the photophysiology and biogeochemistry of the benthic species and their relative abundances.

In the following section, a mechanistic model of the biological drivers of carbon fluxes on coral reefs is first presented. It is then extended to a simplified framework for carbon fluxes coupled with a simple advective transport process across a reef system to explore the changes in water chemistry in downstream habitats (back-reef areas). To provide an experimental basis for the model, we calibrated calcification vs.  $\Omega_a$  curves for both coral-dominated (colonies of branching *Acropora*) and macroalgal-dominated assemblages (*Chnoospora* sp.) on a base substrate of coral sand, using a flume system. Secondly, based on the flume data, a set of model projections was run to examine how varying relative abundances of corals and non-calcifying macroalgae on sand drive carbon chemistry patterns in downstream waters. Lastly, a series of sensitivity analyses were run under simulated  $\text{CO}_2$ -enrichment scenarios to address the question: how will benthic carbon fluxes on reefs interact with anthropogenic ocean acidification? Specifically, we here examine the extent to which coral and algal communities may exacerbate or ameliorate ocean acidification impacts in downstream habitats.

## Model development

A Lagrangian modelling approach was used to explore how physiological and biogeochemical reef processes drive benthic carbon fluxes, effectively simulating the chemical interactions between the reef surface and a water parcel as it moves across the reef. For shallow water reef areas without high structural complexity, a Lagrangian approach is suitable as water transport across the system is predominantly by advection (i.e. low dispersivity, Falter *et al.*, 2008). Two coupled differential equations were set up to describe the uptake or release of  $\text{CO}_2$  (i.e. net community production as the balance between gross community photosynthesis and respiration) and the change in the carbonate ion concentration  $[\text{CO}_3^{2-}]$  as a function of calcification and dissolution. Changes in the carbon chemistry of the reef water were characterized by two key state variables: total dissolved inorganic carbon,  $C_T$ , and total alkalinity,  $A_T$ . This parameter pair, along with temperature and salinity, allows calculation of all other parameters of the marine carbon system (Dickson *et al.*, 2007), including  $\text{pCO}_2$ ,  $\text{pH}_{\text{SW}}$  (seawater scale) and carbonate ion concentrations. Hence,

$$\frac{dC_T}{dt} = -p_n - g_n \quad (1)$$

$$\frac{dA_T}{dt} = -2g_n \quad (2)$$

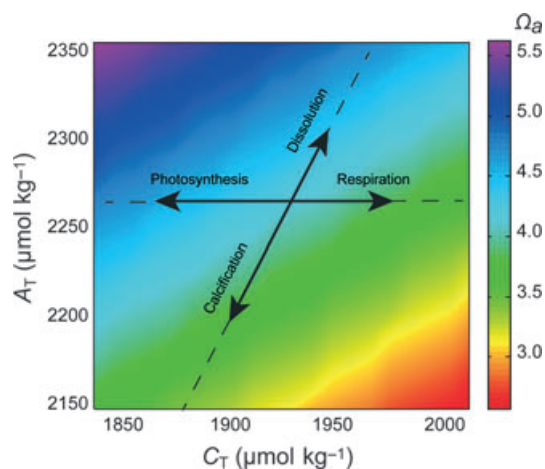
where  $p_n$  is the net rate of photosynthesis (organic productivity) and  $g_n$  is the net rate of calcification. The contribution of  $g_n$  to  $C_T$  (Eqn 1) is based on the fact that 1 mol of  $C_T$  is consumed for every mole of calcium carbonate ( $\text{CaCO}_3$ ) produced (Gattuso *et al.*, 1995). For wind speeds ranging from 2 to 10  $\text{m s}^{-1}$ , the air-sea  $\text{CO}_2$  flux is only 0.1–2.0  $\text{mmol m}^{-2} \text{h}^{-1}$  (Wanninkhof, 1992), and was thus omitted in the analyses.

The change in total alkalinity ( $A_T$ , Eqn 2) is a direct measure of net calcification and dissolution of  $\text{CaCO}_3$  (Kinsey, 1978; Barnes, 1983; Chisholm & Gattuso, 1991) and is not affected by the uptake or production of  $\text{CO}_2$  via photosynthesis and respiration (Smith & Key, 1975; Barnes, 1983). The stoichiometry of alkalinity change as a function of calcification is set at 2 : 1 because two equivalents of total alkalinity (2 mol of bicarbonate or 1 mol of carbonate) are taken out of solution for every mole of  $\text{CaCO}_3$  deposited (Smith & Key, 1975). The changes in  $C_T$  and  $A_T$  are here used as a framework for exploring the relative importance of particulate inorganic carbon production (net calcification) vs. particulate organic carbon production (net photosynthesis) in driving seawater carbon chemistry changes as a function of its residence time over reefs (Fig. 1).

To estimate net community photosynthesis,  $p_n$ , the maximum net rate of photosynthesis,  $p_{\text{max}}$ , and the rate of dark (night) respiration,  $r_{\text{dark}}$ , were used:

$$p_n = p_{\text{max}}(1 - \exp(-E/E_k)) - r_{\text{dark}}, \quad (3)$$

where  $E$  is irradiance (in  $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ ) and  $E_k$  is the level at which photosynthesis begins to saturate. Although studies have shown varying relationships between  $\text{pCO}_2$  (or  $\text{pH}_{\text{SW}}$ ) and primary productivity of corals (Reynaud *et al.*, 2003) and macroalgae (Delgado & Lapointe, 1994; Gattuso



**Fig. 1** Relationship between aragonite saturation state ( $\Omega_a$ ), total dissolved inorganic carbon ( $C_T$ ) and total alkalinity ( $A_T$ ). Arrows and dashed lines indicate directions of changes in  $A_T$  and  $C_T$  caused by calcification, dissolution, photosynthesis and respiration.

*et al.*, 1995), we use a parsimonious model that assumes that primary productivity and respiration are invariant to  $p\text{CO}_2$  (and  $p\text{H}_{\text{SW}}$ ). Values of  $p_n$  are often given as changes in dissolved oxygen concentrations; but they are here converted to  $\text{CO}_2$  at a ratio of 1 : 1 (assuming a photosynthetic quotient of 1, Muscatine, 1990).

Calcification rate is generically expressed as

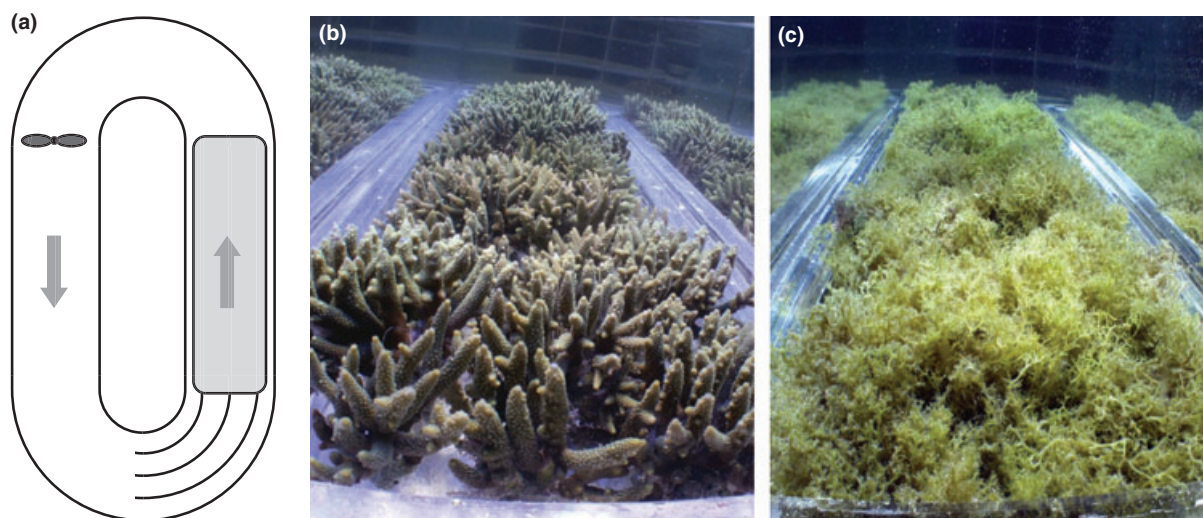
$$g_n = k(\Omega_a - 1)^n - d, \quad (4)$$

where  $k$  is a rate function and  $n$  is the reaction order, both sensitive to temperature (Burton & Walter, 1987; Silverman *et al.*, 2009), and  $d$  is the rate of dissolution. Values for the parameter  $n$  range from below 1 to above 3 across experimental studies

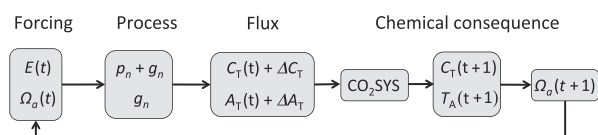
using isolated corals or reef assemblages (Langdon *et al.*, 2000; Langdon & Atkinson, 2005; Schneider & Erez, 2006; Silverman *et al.*, 2007). To formally calibrate Eqn (4) for coral and algal-dominated reef assemblages under controlled light and water flow conditions, a series of flume incubations were conducted for both groups using a wide range of  $\Omega_a$  under both high irradiance and darkness.

### Experimental estimation of calcification parameters

To calibrate day and night calcification rates as functions of  $\Omega_a$  for both coral- and algal-dominated assemblages on sand, we set up a series of flume runs simulating Lagrangian water transects. The flume is a 550-l recirculating Perspex raceway (2.4 m long by 1.2 m wide) with a 0.38 m wide by 0.25 m deep channel (Fig. 2a) stationed on Heron Island (southern Great Barrier Reef, Australia). Colonies of the intertidal branching coral *Acropora aspera* were collected at the outer reef flat and re-established in a sunken floor (0.1 m deep, 0.3 cm wide and 1.2 m long) in the downstream working section of the flume (Fig. 2b). These assemblages represent 100% coral cover, a maximum ratio of 3-dimensional to planar surface area, and hence maximize coral calcification rate per unit area of reef. In the flume, coral colonies were established on a 3 cm thick base of reef sand collected from their native habitat. Similarly, to provide estimates of macroalgal productivity under maximum cover and biomass, assemblages of the common and locally abundant species *Chnoospora* sp. were transplanted from the reef flat to the flume, also positioned on a 3 cm thick base of sand (Fig. 2c). Aragonite saturation state ( $\Omega_a$ ) was manipulated by bubbling  $\text{CO}_2$ -free (0 ppm) or  $\text{CO}_2$ -enriched (~2000 ppm) air into a 2000-l storage tank over a conditioning period of 6–8 h. The partial pressure of dissolved  $\text{CO}_2$  was measured using a submerged  $\text{CO}_2$ -permeable, coiled silicone tube (4 mm diameter, 10 m long) connected in a closed loop to an infrared  $\text{CO}_2$  sensor and recording system (Vaisala GMP343/



**Fig. 2** Diagram of flume (top view) used for carbon flux studies (a). The sunken working section (grey area) measures 0.3 m by 1.2 m. Reef flat communities of *Acropora aspera* (b) and macroalgae (*Chnoospora* sp., c) were used in flume runs to estimate maximum rates of daytime and nighttime productivity (Eqn 3) and to calibrate calcification vs.  $\Omega_a$  response curves (Eqn 4). Corals and macroalgae in the flume were positioned on a bed of sand (3 cm thick) to mimic their native habitat.



**Fig. 3** Conceptual schematic of the discretization of the flux model in which Eqn (1) and (2) use light,  $E$ , and aragonite saturation state,  $\Omega_a$ , as input functions. At each time step (1 min), fluxes in  $\text{CO}_2$  and  $A_T$  are used as input into  $\text{CO}_2\text{SYS}$  to update the distribution on carbon species,  $\text{pH}_{\text{SW}}$  and  $\Omega_a$ .

MI70). Flow velocity in the flume was set to 8–10  $\text{cm s}^{-1}$  and driven by an electrical outboard motor (WaterSnake 34 lb; Jarvis Marine, Dandenong, Australia) connected to a 12 V regulated power supply (Amtek, Meadowbank, Australia). Collimators were installed upstream of the working section of the flume to reduce turbulence, which was verified by near-linear particle tracks in the midstream water above the assemblages. Calcification rate was estimated using the alkalinity anomaly method based on water samples (500 ml) taken at the beginning and end of 1–2 h incubations. Samples were poisoned immediately using 200  $\mu\text{l}$  of concentrated  $\text{HgCl}_2$ .  $A_T$  was determined by Gran titration (Dickson *et al.*, 2003) using a Mettler-Toledo (T50) system. Organic productivity was estimated based on differences in total dissolved inorganic carbon and alkalinity as  $p_n \sim dC_T/dt + dA_T/dt$  (Gattuso *et al.*, 1995). Based on the water flow speed (8–10  $\text{cm s}^{-1}$ ) and a relatively stagnant air space above the flume, air-water  $\text{CO}_2$  exchange was  $<0.2 \text{ mmol m}^{-2} \text{ h}^{-1}$ . For daytime runs, the corals were illuminated by two metal halide lamps ( $2 \times 150 \text{ W}$ ; AquaMedic, Bissendorf, Germany) delivering down-welling irradiance of  $\sim 1000 \mu\text{mol m}^{-2} \text{ s}^{-1}$  at the level of the assemblages, measured by a Li-192s underwater light sensor (LiCor, Lincoln, NE, USA). Each community type was run as duplicates or triplicates using new assemblages for each series. Flume runs without benthic communities showed  $<1\%$  change in  $C_T$  and  $A_T$  over a 4-h incubation period for non-acidified conditions. At high  $\text{CO}_2$  concentrations (600 and 900 ppm),  $C_T$  changed around 5%, which was corrected for in the analyses. Parameter values for the daytime and nighttime calcification rates vs.  $\Omega_a$  responses were estimated by fitting Eqn (4) to the pooled data using least-squares (Levenberg–Marquardt algorithm) non-linear regression (programmed in MatLab 7.10; MathWorks, Natick, MA, USA).

## Model projections

Three sets of simulations were run to address each of the following questions. First, to explore how coral-dominated vs. algal-dominated communities modify the carbon chemistry of reef water as a function of residence time in shallow water, the changes in  $\text{pCO}_2$ ,  $\text{pH}_{\text{SW}}$ ,  $A_T$  and  $\Omega_a$  were simulated for water residence times up to 3 h. Experimental flume data were used as input into the carbon flux model (Fig. 3). Simulations were run for both day and night, which enabled analyses of diurnal carbon chemistry variation at fixed residence times. This has implications for temporal as well as spatial carbon chemistry variation across reef systems. Secondly, we analysed how varying

combinations of corals and macroalgal abundance would modify  $\Omega_a$  along tracks of reef water. This provides an insight into the relative importance of reef calcifiers vs. non-calcifying primary producers in driving  $\Omega_a$  patterns. Thirdly, to assess how benthic carbon fluxes on reefs interact with acidification of the ocean source water, we examined to what extent different compositions of corals and algae may exacerbate or ameliorate the exposure of reef habitats to ocean acidification.

For all simulations, a numerical approach was used by converting Eqns (1) and (2) to difference equations with discrete 1-min time intervals (Fig. 3). As the goal was to explore relative contributions from benthic community production and calcification to carbon chemistry changes, and how this compares between community types, the following set of standard conditions was used. First, a water depth of 1 m, representing an average depth at tidal reef flats on the Great Barrier Reef, was used in the model (Barnes, 1983; Hopley *et al.*, 2007). Full vertical mixing was assumed during the 1-min sampling intervals as coral reef habitats generally have a high roughness value (Monismith, 2007). However, the downstream mixing in the shallow water of the flume (0.25 m) was likely to be higher than at 1 m depth on a reef flat, potentially overestimating mixing during the 1-min time intervals between updating the carbon system in the model. Second, the effects of flow velocity on the biogeochemical processes were not explicitly accounted for. Although it is well established that flow velocity influences mass transfer relations in benthic organisms and enhances rates of photosynthesis, respiration and calcification (Patterson *et al.*, 1991; Bilger & Atkinson, 1992; Mass *et al.*, 2010), little data exist for determining flow-adjusted carbon fluxes of individual community types. Thirdly, for the present-day scenario ( $\text{pCO}_2 \sim 400 \mu\text{atm}$ ), the following boundary conditions were used for the carbon chemistry of the open ocean source water before it enters the reef ( $t = 0$ ):  $A_T = 2200 \mu\text{Eq kg}^{-1}$ ,  $C_T = 1950 \mu\text{mol kg}^{-1}$ , temperature = 25 °C and salinity = 35.

Projections for all simulations were based primarily on the detailed carbon fluxes obtained for the coral and macroalgal assemblages on sand assayed in the flume. For both coral and macroalgal communities, simulations were run for water residence periods of 3 h. After each 1-min time interval, rates of net photosynthesis ( $p_n$ ), net calcification ( $g_n$ ) and their error estimates (Table 1) were calculated based on the input variables, irradiance ( $E$ ) and  $\Omega_a$  for each species group. The resulting changes in  $A_T$  and  $C_T$  were then used to calculate shifts in the carbon system using the shareware  $\text{CO}_2\text{SYS}$  (Lewis & Wallace, 1998). The output  $\Omega_a$  from  $\text{CO}_2\text{SYS}$  was then used as input for the calcification response of the subsequent time step. The simulation procedure is outlined in Fig 3. Although net community calcification generally scales positively with gross community primary production (Gattuso *et al.*, 1999), preliminary analyses of the flume data indicated that rate of coral photosynthesis did not correlate significantly with  $\Omega_a$  or rate of calcification, and was thus omitted as a functional response. To account for variation in the benthic flux parameters influencing carbon chemistry profiles as a function of residence time, simulations were repeated 1000 times as Monte Carlo analyses. Specifically, for each simulation of a species group, parameter values for photosynthesis and calcification were sampled from within the



**Table 1** Summary results of productivity and calcification parameters for flume runs (1–2 h incubations at  $10 \text{ cm s}^{-1}$ ) using mono-specific assemblages of corals (*Acropora aspera*) and macroalgae (*Chnoospora* sp.) on a bed of sand (Fig. 2). Data are estimates and their standard deviations derived from non-linear regressions for 2–3 replicate flume runs. See text for method details. Values for parameters  $k$  and  $n$  were estimated by fitting Eqn (4) to the calcification vs.  $\Omega_a$  data using non-linear least-squares regression. For corals (*A. aspera*), dissolution was omitted, forcing the fit through ( $\Omega_a -1, 0$ ), as  $d$  was not significantly different from zero in preliminary analyses

Parameter	Species	Estimate	Unit
$p_{\text{max}}$ – Maximum net rate of photosynthesis (at irradiance $\sim 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ , Eqn 2)	<i>Acropora aspera</i>	$79 \pm 7$	$\text{mmol m}^{-2} \text{h}^{-1}$
	<i>Chnoospora</i> sp.	$96 \pm 6$	
$r_{\text{dark}}$ – Nighttime rate of respiration (Eqn 2)	<i>A. aspera</i>	$37 \pm 4$	$\text{mmol m}^{-2} \text{h}^{-1}$
	<i>Chnoospora</i> sp.	$13 \pm 8$	
$g_{\text{max}}$	<i>A. aspera</i> – day	$62.8 \pm 2.50$	$\text{mmol m}^{-2} \text{h}^{-1}$
	<i>A. aspera</i> – night	$26.3 \pm 1.50$	
$k$ – Calcification rate function (Eqn 4)	<i>A. aspera</i> – day	$43.8 \pm 3.55$	$\text{mmol m}^{-2} \text{h}^{-1}$
	<i>A. aspera</i> – night	$17.9 \pm 1.50$	
	<i>Chnoospora</i> sp./sand – day	$0.61 \pm 0.32$	
	<i>Chnoospora</i> sp./sand – night	$3.50 \pm 1.10$	
$n$ – Calcification reaction order (Eqn 4)	<i>A. aspera</i> – day	$0.37 \pm 0.12$	Dimensionless
	<i>A. aspera</i> – night	$0.35 \pm 0.10$	
	<i>Chnoospora</i> sp./sand – day	$2.62 \pm 0.52$	
	<i>Chnoospora</i> sp./sand – night	$0.17 \pm 0.60$	
$d$ – Dissolution	<i>A. aspera</i> – day	n/a	$\text{mmol m}^{-2} \text{h}^{-1}$
	<i>A. aspera</i> – night	n/a	
	<i>Chnoospora</i> sp. – day	$4.30 \pm 0.40$	
	<i>Chnoospora</i> sp. – night	10	

normal distributions defined by their means and standard deviations (Table 1).

Lastly, a sensitivity analysis was used to examine the effect of ocean acidification scenarios on relative changes in  $\Omega_a$  across coral, mixed and algal assemblages on sand. This analysis was used to address the specific hypothesis: are ocean acidification effects exacerbated or dampened by benthic carbon flux processes? Here, the total dissolved inorganic carbon ( $C_T$ ) of the ocean source water was set to three values in successive analyses: 1950, 2050 and 2130  $\mu\text{mol kg}^{-1}$  representative of  $p\text{CO}_2$  levels of 400, 600 and 900 ppm. Sensitivity to ocean acidification as a function of residence time was then calculated as the relative change in  $\Omega_a$  profiles between acidified (600 or 900 ppm) and present-day (400 ppm) scenarios. Sensitivity was thus a measure of the extent to which ocean acidification was damped across the reef by benthic carbon fluxes.

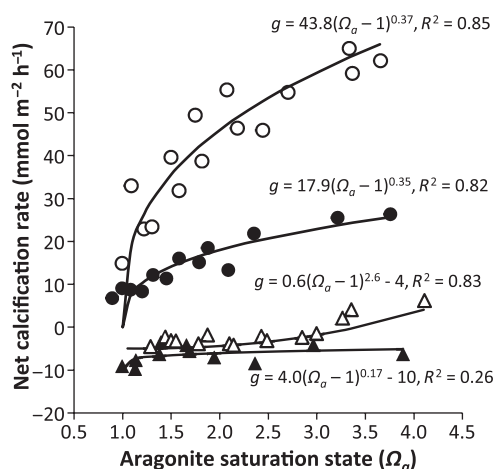
## Results

### Experimental data

The relationship between rate of net calcification,  $g_n$ , and aragonite saturation state,  $\Omega_a$ , for both coral/sand and macroalgae/sand assemblages was represented

well by the calcification model (Eqn 4), with more than 80% of the variation in  $\Omega_a$  explained by the model ( $R^2 = 0.85$ ). For corals (*A. aspera*) on sand, the daytime rate function,  $k = 43.8 \pm 3.5 \text{ mmol m}^{-2} \text{h}^{-1}$ , was 2.5 times that of the nighttime rate,  $k = 17.9 \pm 1.5 \text{ mmol m}^{-2} \text{h}^{-1}$  (Fig. 4, Table 1). Interestingly, daytime and nighttime rates of calcification were both decelerating functions of  $\Omega_a$ , with the value of the reaction order significantly lower than unity ( $n \sim 0.35$ – $0.37$ ). As dissolution,  $d$ , cannot be established from the alkalinity anomaly technique, it was set to  $0 \text{ mmol m}^{-2} \text{h}^{-1}$ , i.e. the calcification response in Fig. 4 was forced through the point ( $\Omega_a -1, 0$ ). The maximum daytime rate of coral net calcification (at  $\Omega_a \sim 4$ ) was  $62.8 \pm 2.5 \text{ mmol m}^{-2} \text{h}^{-1}$ , and the nighttime rate of net calcification was approximately 40% of the day rate (maximum  $g_n = 26.3 \pm 1.5 \text{ mmol m}^{-2} \text{h}^{-1}$ ).

For the macroalgal assemblage (*Chnoospora* sp.), the calcification/dissolution signal was driven entirely by processes in the sand, which were dominated by net dissolution (Fig. 4). For low values of  $\Omega_a$ , the net dissolution rate was approximately  $10 \text{ mmol m}^{-2} \text{h}^{-1}$ , which was used to set the value for the term  $d$  in the regres-



**Fig. 4** Relationship between net rate of calcification ( $g_n$ ) and aragonite saturation state ( $\Omega_a$ ) for dense assemblages of corals (*Acropora aspera*, circles) and macroalgae (*Chnoospora* sp., triangles) on sand in flume incubations. The modelled responses (line) were obtained by fitting Eqn (3) to the calcification data using non-linear regression. Open symbols are for daytime rates at high irradiance ( $E \sim 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ ) and filled symbols are for night rates. The dissolution rate,  $d$ , was set to 0 for corals as estimates could not be determined by the regression. The dissolution rate of the macroalgae/sand assemblage was set to  $10 \text{ mmol m}^{-2} \text{h}^{-1}$  consistent with observed night rates near  $\Omega_a = 1$ . See Table 1 for errors (standard deviations) associated with parameter estimates.

sions of Eqn (4). Daytime calcification of the *Chnoospora*/sand assemblage showed a significant response to  $\Omega_a$ , which was well explained by Eqn (4) ( $R^2 = 0.83$ ). At night, however, dissolution rates varied within a narrow range of  $5\text{--}10 \text{ mmol m}^{-2} \text{h}^{-1}$ , resulting in a non-significant fit for the regression (Fig. 4). Additional flume runs for the sand bed without corals or macroalgae resulted in  $g$  vs.  $\Omega_a$  responses similar to those of the *Chnoospora*/sand assemblage (not shown), indicating that the cover of macroalgae was not a significant barrier for carbonate fluxes between sand and water at the flow speed used ( $8\text{--}10 \text{ cm s}^{-1}$ ). Maximum rates of gross community production, estimated from calcification rates and changes in  $C_T$  under high irradiance, was approximately 20% higher for the *Chnoospora* sp. ( $p_{\text{max}} = 96 \pm 6 \text{ mmol m}^{-2} \text{h}^{-1}$ ) compared with the *Acropora* ( $p_{\text{max}} = 79 \pm 7 \text{ mmol m}^{-2} \text{h}^{-1}$ ) assemblage (Table 1).

#### Model projections – carbon chemistry variation as a function of residence time

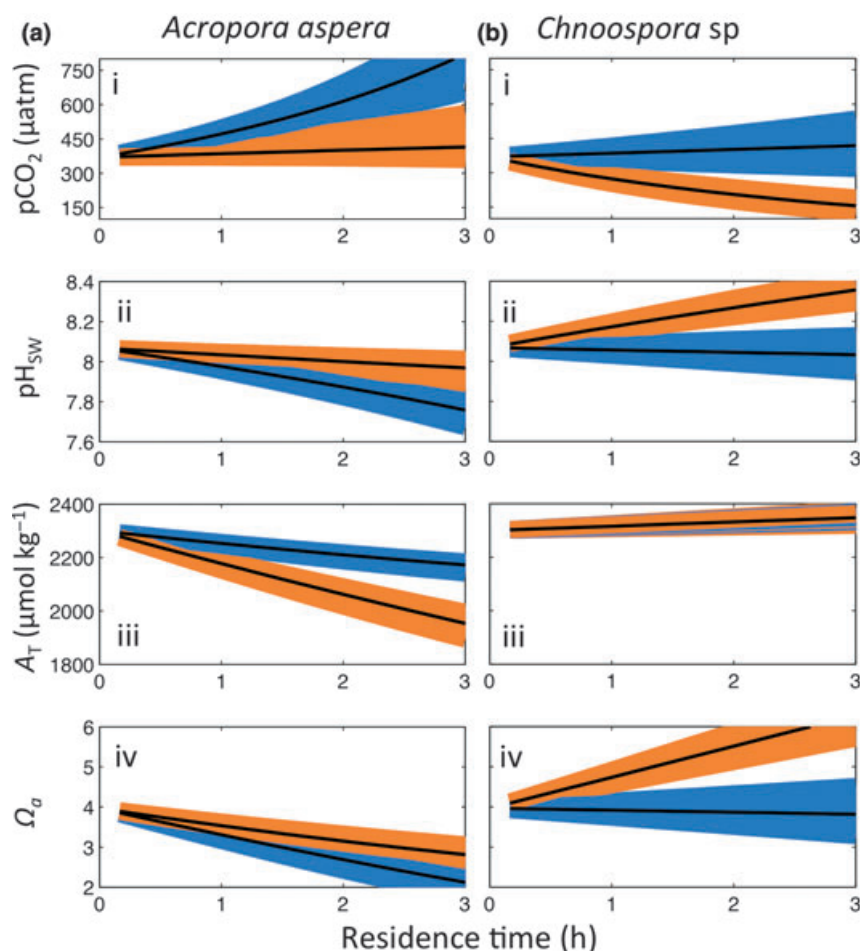
Projections for seawater carbon chemistry parameters as a function of residence time showed strong differences between corals and macroalgae. This was

demonstrated experimentally in flume incubations as well as analytically for 3-h simulations of daytime and nighttime carbon fluxes. For corals, the changes in carbonate chemistry during the day due to calcification and community production resulted in only minor changes in  $p\text{CO}_2$  (orange band in Fig. 5ai) and caused only a minor drop in  $\text{pH}_{\text{SW}}$  (seawater scale) from around 8.1 to 8.0 (Fig. 5aii). However, calcification, as indicated by the decline in total alkalinity (Fig. 5aiii) led to a drop in  $\Omega_a$  from 4 to below 3 (Fig. 5aiv). At night, coral calcification and respiration led to a near doubling of  $p\text{CO}_2$  (blue band in Fig. 5ai) and a drop in  $\text{pH}_{\text{SW}}$  from 8.1 to below 7.8 (Fig. 5aii) of the reef water during the 3 h residence period. The nearly 50% drop in  $\Omega_a$  of the water over corals at night (from 4 to 2, blue band in Fig. 5aiv) was driven by dark calcification and net respiration – partly due to a net increase in  $p\text{CO}_2$ .

In contrast, the high net productivity of the non-calcifying macroalgal/sand assemblage during the day led to a significant drawdown of  $p\text{CO}_2$  (Fig. 5bi). Specifically, over a simulated 3-h period during the day,  $p\text{CO}_2$  was reduced from around 400 to below  $200 \mu\text{atm}$ , consistent with observations for long flume trials. Consequently,  $\text{pH}_{\text{SW}}$  rose from 8.1 to almost 8.4 (Fig. 5bii). The small increase in alkalinity with residence time (Fig. 5biii) was caused by dissolution of the sand bed. These changes in  $p\text{CO}_2$  and  $\text{pH}_{\text{SW}}$  led to a dramatic increase in  $\Omega_a$ , from 4 to around 6 after 3 h (Fig. 5biv). Patterns of carbon chemistry change at night were much smaller for the dense macroalgae/sand compared with those for the coral/sand assemblage for two reasons. First, despite a large algal biomass ( $235 \text{ g dry weight m}^{-2}$ ), the rate of dark respiration for the macroalgae was only a third that of the corals (Table 1). Secondly, a high rate of calcification at night for the corals led to a drop in the carbonate ion concentration, driving up  $p\text{CO}_2$  and lowering  $\Omega_a$  (Fig. 5biv).

#### Effect of coral vs. macroalgal abundance on $\Omega_a$ profiles

To further explore the relative contribution of calcifying vs. non-calcifying primary producers to patterns of aragonite saturation state as a function of residence time, we set up a simulation in which the relative abundance of corals and macroalgae was varied reciprocally between 0 and 1, respectively, with the sum of the two equal to unity – i.e. 100% benthic cover by corals and/or macroalgae on sand (Fig. 6). This projection enabled analyses of the effect of changing community composition on seawater carbon chemistry patterns downstream. Effects of space competition on algal or coral metabolism or calcification were not considered, as *Chnoospora* does not elicit a stress response in *Acropora* (Guillermo Diaz-Pulido, personal communication).



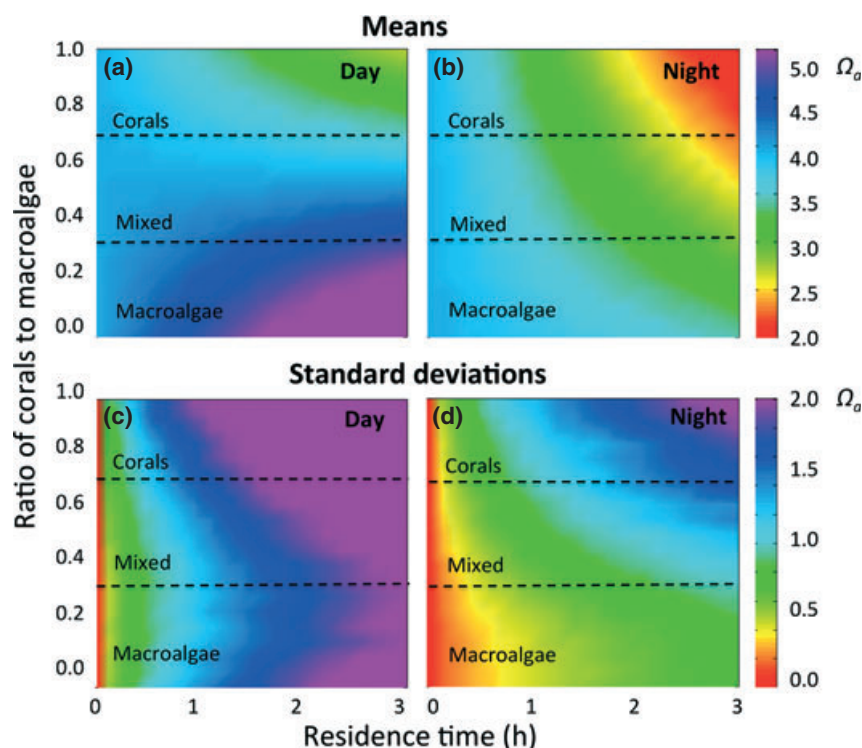
**Fig. 5** Modelled profiles of  $pCO_2$ ,  $pH_{sw}$  (seawater scale), total alkalinity and aragonite saturation state as a function of residence time at 1-m water depth across dense (Fig. 3) assemblages of corals (*Acropora aspera*, a) and macroalgae (*Chnoospora sp.*, b). Orange bands are confidence envelopes for day simulations (Monte Carlo analyses) and blue bands are for night simulations. Black lines are for the projection using mean parameter estimates in Table 1.

Parameter values and standard/boundary conditions [i.e. depth = 1 m,  $T = 27^\circ C$ ,  $S = 35$ ,  $C_T(t = 0) = 1950$  and  $A_T(t = 0) = 2200$ ] were similar to those used to generate simulations in Fig. 5 (see also Table 1). Results showed that for an assemblage composed of a mixture of dense clones of corals (*A. aspera*) and macroalgae (*Chnoospora sp.*), the strong drawdown of  $CO_2$  by macroalgal (and coral) photosynthesis and carbonate ion drawdown by daytime calcification (by corals) counteract each other to the extent that the predicted  $\Omega_a$  only shows minor variation with residence time (blue isocline in Fig. 6a). At night, all combinations of corals and macroalgae led to a drop in  $\Omega_a$ . Specifically, for coral assemblages without macroalgae, high rates of night calcification and respiration lowered  $\Omega_a$  to around 2 after 2–3 h (Fig. 6b), consistent with simulations in Fig. 5biv. For gradual increases in macroalgal abundance, the drop in  $\Omega_a$  was reduced proportionately,

due to lower rates of dark respiration and lack of night calcification by the macroalgae (Fig. 6b). Reducing the abundances of corals and macroalgae in additional simulations (i.e. increasing the relative area of exposed sand, not shown) dampened the predicted pattern of  $\Omega_a$  variation proportionately as the calcification/dissolution response of sand (isolated and under coral/macroalgal assemblages) was <20% of the calcification response of corals within the  $\Omega_a$  range 1–4.

#### *Sensitivity of $\Omega_a$ patterns to ocean acidification*

Simulations of  $\Omega_a$  as a function of residence time under a present-day  $CO_2$  regime as well as under two ocean acidification scenarios (400, 600 and 900 ppm  $CO_2$  respectively) indicated that patterns of  $pCO_2$  change only marginally across dense coral assemblages during the



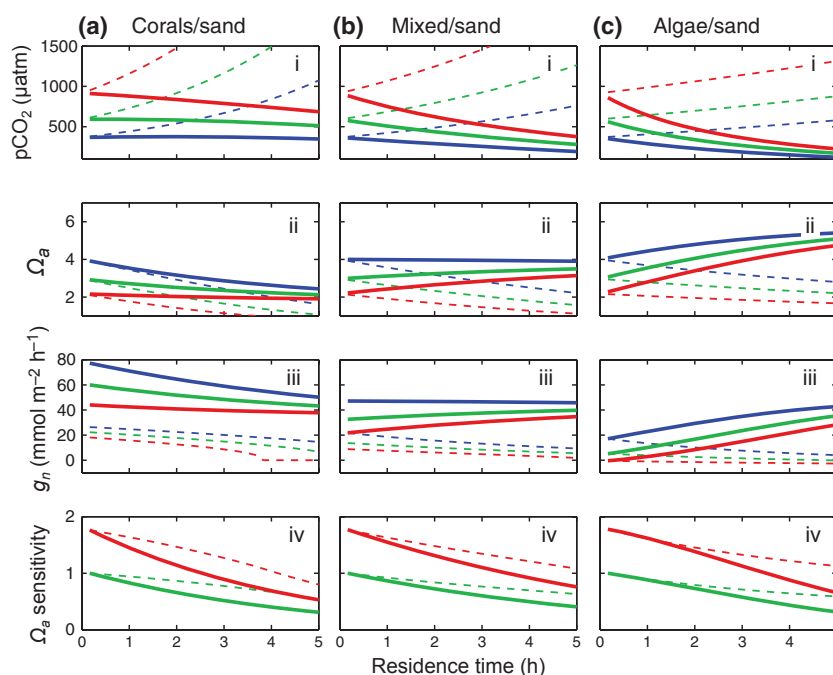
**Fig. 6** Profiles of aragonite saturation state (a: means; b: standard deviations) as a function of the relative abundance (% cover) of corals (*Acropora aspera*) and macroalgae (*Chnoospora* sp.) and residence time. Standard deviations were obtained by Monte Carlo analysis in which parameter estimates (Table 1) were sampled 1000 times from within their normal distributions.

day, regardless of the acidification scenario (Fig. 7ai). During the night, ocean acidification is strongly enhanced by respiration (dashed lines). In contrast, mixed assemblages set to 50% cover of corals (*Acropora aspera* on sand) and 50% cover of macroalgae (*Chnoospora* sp. on sand) drove  $\text{CO}_2$  levels in downstream waters to less than half the ocean  $\text{CO}_2$  level in <3 h (Fig. 7ai and bi). The daytime depletion in  $\text{pCO}_2$  over the mixed and macroalgal communities for the 600 and 900 ppm acidification scenario led to both  $\Omega_a$  and the rate of coral calcification to increase as functions of residence time (Fig. 7bii and iii). At night, this pattern was reversed. Interestingly, daytime patterns of  $\Omega_a$  converged with increasing residence time for corals, mixed assemblages and macroalgae (Fig. 7aai, bai, cai). The primary driver of this pattern was the suppressed rates of calcification (i.e. smaller changes in  $A_T$ ) in upstream waters under the ocean acidification scenarios (Fig. 7aiii, biii), feeding back to a slower decline in  $\Omega_a$  with residence time. Consequently, although  $\Omega_a$  is highly sensitive to  $\text{CO}_2$  enrichment during the day at low residence times (i.e. near the ocean source water), this sensitivity declined rapidly with residence time under the most severe ocean acidification scenario (red line in Fig 7aiv).

## Discussion

The results of this study demonstrate two key points. First, the benthic composition of calcifying vs. non-calcifying primary producers can play a key role in driving the carbon chemistry of shallow reef waters. In particular, high daytime rates of net photosynthesis by benthic algae can improve the chemical conditions for reef calcification in downstream habitats. Secondly, the high ratio of benthic to air-sea carbon fluxes on reefs is likely to dampen the ocean acidification signal during the day, but amplify the signal at night, as water moves from reef front to back-reef habitats. This has significance for how back-reef or lagoonal reef waters will be exposed to ocean acidification, in particular if upstream communities change in their relative abundance of calcifying (e.g. corals) and non-calcifying (e.g. turfs or fleshy algae) benthic groups. In the following section, we address the biological, biogeochemical and physical/chemical drivers underlying these findings, and then discuss how the coupled benthos-seawater carbon flux model can provide insight into patterns of reef exposure to ocean acidification.





**Fig. 7** Effect of ocean acidification ( $\text{CO}_2$  enrichment) scenarios on the profiles of  $\text{pCO}_2$ , aragonite saturation state,  $\Omega_a$ , calcification rate and sensitivity of  $\Omega_a$  profiles for (a) coral-dominated (100% cover of *Acropora aspera*), (b) mixed coral (50%) and macroalgal (*Chnoospora* sp., 50%) assemblages, and (c), macroalgae only (100% cover of *Chnoospora*). Solid lines are for daytime and dashed lines for nighttime projections.  $\text{CO}_2$  scenarios are represented by the following colour coding: blue 400 ppm, green 600 ppm and red 900 ppm. Sensitivity of  $\Omega_a$  was calculated as the change in  $\Omega_a$  at a given residence time point due to ocean acidification, relative to the change in  $\Omega_a$  of the ocean source water (at  $t = 0$  min) due to ocean acidification.

#### Benthic drivers of carbon chemistry variation

High rates of calcification by coral assemblages (here *A. aspera*) can significantly lower the aragonite saturation state ( $\Omega_a$ ) in downstream habitats. In contrast, the net  $\text{CO}_2$  drawdown during the by non-calcifying algae (as exemplified here by *Chnoospora* sp.) can reverse that pattern (Figs 5 and 6). Consequently, areas with high algal abundance and a high ratio of organic to inorganic productivity can potentially promote calcification rates in downstream waters, depending on water depth and how long the reef water resides over algal assemblages. As our model projections are built on parameters for only three components of reef communities (corals, macroalgae and sand) assayed in a flume environment, they are not intended to predict carbon flux patterns across reef systems *in situ*. These analyses are extended in a companion paper to investigate how mixed assemblages *in situ* modify carbon chemistry patterns on a reef system (Kleypas *et al.*, 2011). The controlled system's approach of this study, however, enables a detailed first-order analysis of the feedbacks between carbon flux processes of key benthic groups and seawater carbon chemistry patterns, and how these are likely to interact with ocean acidification. Interestingly, the lack of variation

between the  $g_n$  vs.  $\Omega_a$  response of dense *Chnoospora* assemblages on sand compared with the response of sand in isolation indicated that the mass transfer of inorganic carbon between water column and sand bed was not reduced significantly by the algal layer at the experimental flow speed of  $8\text{--}10\text{ cm s}^{-1}$ . Tentatively, this result provides the basis for a prudent extension of model projections to assemblages with lower percentages of coral and macroalgal cover – i.e. the contribution from corals and macroalgae can be scaled to their relative areal abundances.

The curvilinear calcification vs.  $\Omega_a$  response function of the coral assemblage used in this study is consistent with other studies for individual coral species (e.g. Gattuso *et al.*, 2000; Marubini *et al.*, 2001; Anthony *et al.*, 2011). Specifically, the reaction order (exponent  $n$ ) for *A. aspera* was significantly less than unity (0.35–0.37), almost an order of magnitude less than the value (2.1–3.2) reported by Silverman *et al.* (2007) for mixed reef assemblages. A curvilinear (decelerating) calcification vs.  $\Omega_a$  response signifies a higher rate of calcification at low carbonate ion concentrations than predicted from an inorganic precipitation vs.  $\Omega_a$  relationship (Burton & Walter, 1987). Variation in the shape of the  $g_n$  vs.  $\Omega_a$  response curve influences the feedbacks between

seawater carbon chemistry and calcification along the residence time axis. Specifically, for a calcifying reef community, a curvilinear (i.e.  $n < 1$ )  $g_n$  vs.  $\Omega_a$  response signifies a small  $\Omega_a$  change per unit time (or distance) in areas of high  $\Omega_a$  and a large  $\Omega_a$  change in areas of low  $\Omega_a$ . Other studies have reported linear or accelerating  $g_n$  vs.  $\Omega_a$  relationships for mixed reef communities ( $n > 2$ , Silverman *et al.*, 2007;  $n = 1$ , Andersson *et al.*, 2009), which would signify opposite  $\Omega_a$  dynamics. The curvilinear relationship for the  $g_n$  vs.  $\Omega_a$  response curve for the coral community used here (Fig. 4), which is consistent with those reported for other single-species assays for corals (Gattuso *et al.*, 2000; Marubini *et al.*, 2001), may thus be underestimating  $\Omega_a$  changes in upstream (e.g. reef front) water, but overestimating  $\Omega_a$  changes in downstream (e.g. back reef or lagoonal) areas. However, additional analyses using linear ( $n = 1$ ) and accelerating ( $n > 2$ ) calcification responses produced qualitatively similar  $\Omega_a$  changes over a long residence period.

#### *Implications for temporal and spatial patterns of carbon chemistry variation*

One implication of the contrasting effects of corals and macroalgae on  $\Omega_a$  and  $\text{CO}_2$  dynamics (Figs 5 and 6) is that high daytime calcification rates in coral dominated zones on the crest and outer reef flat (Kinsey, 1985) may occur at the expense of reduced conditions for calcification in downstream (e.g. back-reef) areas as carbonate ion concentrations and  $\Omega_a$  are reduced by upstream communities. Environmental factors other than carbonate chemistry also distinguish reef fronts from back reef and lagoonal areas, including temperature (McCabe *et al.*, 2010) and water motion (Symonds *et al.*, 1995). However, the strong diurnal and spatial variations in  $\text{pH}_{\text{SW}}$  (7.8–8.5) and  $\Omega_a$  (2–6) observed across Heron Reef (Anthony *et al.*, 2008) demonstrate that carbon chemistry variation is another key factor separating upstream and downstream habitats. The contrast between daytime and nighttime carbon chemistry patterns at long residence times illustrates that downstream habitats on some reefs may experience fluctuations in  $\text{pCO}_2$  ranging from preindustrial to projected end-of century atmospheric levels over the course of 24 h (Santos *et al.*, 2011). The significance of such diurnal variation for the function of reef communities is unknown, but may suggest contrasts in the biogeochemical challenges of reef communities in back-reef or lagoonal vs. reef-front habitats.

#### *Implications for impacts of ocean acidification*

Comparisons of projections for  $\text{pCO}_2$  and  $\Omega_a$  under the two ocean acidification scenarios indicated two signifi-

cant patterns. First, daytime  $\text{pCO}_2$  profiles will not change greatly as acidified water flows over dense coral communities, and the decline in  $\Omega_a$  will lessen as water moves downstream. The latter is explained by a decline in calcification rate feeding back to a slower decline in  $\Omega_a$ . At night, net respiration by the reef community leads to further acidification of the ocean source water, exacerbating ocean acidification exposure in downstream habitats. Secondly, daytime macroalgal productivity will dampen the ocean acidification influence through a drawdown in  $\text{pCO}_2$  as well as by increasing  $\Omega_a$ . The lower respiration rate of macroalgae relative to corals leads to less extreme nighttime acidification in downstream habitats. For large reef systems with long water residence times (Black *et al.*, 1990), the extent to which downstream habitats will be exposed to ocean acidification impacts will thus depend on community composition upstream, reef bathymetry, water circulation patterns and to what extent organic material is exported from or retained in the system. Importantly, however, this comparison does not account for the prediction that coral-dominated communities are likely to shift towards increasing dominance of macroalgae as atmospheric  $\text{CO}_2$  concentrations increase (Hoegh-Guldberg *et al.*, 2007; Anthony *et al.*, 2011; Diaz-Pulido *et al.*, 2011). Under such community shifts, the ratio of organic to inorganic carbon production may increase in areas exposed to acidified ocean waters, but potentially enhance the dampening of ocean acidification influences as the water moves downstream across the reef. The extent to which the organic carbon accumulated in macroalgae is remineralized within the system or transported off the reef (for example by grazing fish) will play a key role in determining the net impact on reef water carbon chemistry.

#### *Limitations/strengths of study species comparison and flume environment*

The branching coral (*A. aspera*) and macroalgal (*Chnoospora* sp.) species used in this study are representatives of spatial dominants of reef flat communities on parts of the Great Barrier Reef. Using dense monospecific stands of these species (both having high ratios of 3-dimensional to planar surface areas) in a controlled flume environment enabled us to provide first-order estimates of maximum contributions of benthic calcification and photosynthesis to changes in the carbon chemistry of reef waters. We acknowledge that the partitioning of carbon fluxes is likely to be more complicated within natural, more diverse benthic reef communities (such as those examined by Barnes, 1983; Gattuso *et al.*, 1996). However, as *A. aspera* on Heron reef flat mostly occurs in 1–10 m large clones separate from patches of the macroalga (*Chnoospora*) on sandy areas,  $\Omega_a$

projections for mixed coral/algal/sand communities based on assays for individual groups are well represented. Interestingly, the maximum rate of calcification for the flume assemblages of *A. aspera* ( $65 \text{ mmol m}^{-2} \text{ h}^{-1}$ ) was approximately 2–3 times those reported for Lagrangian-based measurements of natural reef communities (Barnes, 1983; Gattuso *et al.*, 1996), consistent with approximate differences in percent coral cover.

## Conclusions

In summary, benthic communities in shallow-water coral reef systems can strongly modify the seawater carbon chemistry depending on net rates of calcification, primary production and residence time. The direction of changes in aragonite saturation state ( $\Omega_a$ ) of the reef water is thus largely governed by the composition of calcifiers and primary producers. Whereas corals with high productivity and calcification rates reduce  $\Omega_a$ , high rates of net photosynthesis by macroalgae or other non-calcifying primary producers can raise  $\Omega_a$  significantly during the day, effectively improving the conditions for calcification in downstream habitats. Benthic processes will not buffer reef areas exposed directly to ocean source water. However, for reef systems with long residence times (e.g. large systems), ocean acidification impacts will be exacerbated in downstream habitats by calcification and respiration, but ameliorated by photosynthesis and dissolution. Lastly, a shift in reef community composition from coral to algal dominance in upstream areas under ocean acidification will potentially improve conditions for calcification in downstream areas, depending on water residence time, bathymetry and circulation patterns.

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